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Assessing Comparative Terrestrial Ecotoxicity of Cd, Co, Cu, Ni, Pb, and Zn: The Influence of Aging and Emission Source

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Abstract

Metal exposure to terrestrial organisms is influenced by the reactivity of the solid-phase metal pool. This reactivity is thought to depend on the type of emission source, on aging mechanisms that are active in the soil, and on ambient conditions. Our work shows, that when controlling for soil pH or soil organic carbon, emission source occasionally has an effect on reactivity of Cd, Co, Cu, Ni, Pb and Zn emitted from various anthropogenic sources followed by aging in the soil from a few years to two centuries. The uncertainties in estimating the age prevent definitive conclusions about the influence of aging time on the reactivity of metals from anthropogenic sources in soils. Thus, for calculating comparative toxicity potentials of man-made metal contaminations in soils, we recommend using time-horizon independent accessibility factors derived from source-specific reactive fractions.

Capsule abstract

Improving current life cycle inventory (LCI) and life cycle impact assessment (LCIA) practice in terrestrial ecotoxicity assessment of metals.

1. Introduction

Life cycle assessment (LCA) is used to quantify the potential environmental impacts of goods and services (ISO, 2006). The life cycle inventory (LCI) phase of the LCA quantifies the flows of resource consumptions and emissions that are associated with the good or service (e.g., the generation of 1 kWh of electricity to the grid from a pulverized coal power plant), when considering all the processes that are involved in the whole underlying life cycle. In the life cycle impact assessment (LCIA) phase these input and output flows are translated into potential environmental impacts using substance-specific characterization factors (CF) (Hauschild, 2005). CFs are also referred to as comparative toxicity potentials (CTP) for those impacts that are related to chemical pollution. CTPs should be seen as relative performance indicators and must ensure a fair comparison between substances in terms of their potential impact on an ecosystem (Hauschild and Huijbregts, 2015). In this paper, we address two limitations of the current LCI and LCIA practice of terrestrial ecotoxicity assessment of metals, namely: (i) the reporting of anthropogenic metal emissions based on their elemental content and oxidation stage, ignoring potentially relevant information about the emission sources (e.g., deposition to soil of an airborne emission of a metal in fly ash vs. direct emission to soil of a metal in a coal slag); and (ii) the disregarding aging of the contamination in the calculation of the CTP values.

The CTP of a substance in soil is calculated as the product of three factors: (i) a fate factor, FF (which expresses the resident mass of the substance in soil per unit of emission flow); (ii) an exposure factor, XF (which represents the bioavailability of the substance to organisms in soil), and (iii) an effect factor, EF (which describes the ecotoxicological impacts on the soil ecosystem) (Henderson et al., 2011). In soils, apart from immediate bioavailability of a metal as influenced by the metal speciation pattern in soil pore water, the potential for metal exposure also depends on the metal's potential to undergo environmental processes (such as dissolution) from the solid phase disposing it for uptake by biota and leaching to deep soil layers or runoff to surface water (Owsianiak et al., 2013). This potential is referred to as accessibility and defined as "the mass quantity of a chemical that is or can become available within a given time span and under given conditions" (Reichenberg and Mayer, 2006). To take into account the influence of the accessible metal pool in the soil, the XF of metals in soils has recently been defined as the product of an accessibility factor, ACF (representing the accessible fraction of the total metal in the soil) and a bioavailability factor, BF (that represents the fraction of the accessible metal in the soil that is present in directly bioavailable, toxic forms) (Owsianiak et al., 2013).

The accessible metal pool is often approximated by “available” metal measured with diffusive gradient in thin films) or by “reactive” metal (also called “labile” or “exchangeable”) measured with single or sequential extraction procedures (SEP) or isotope-based methods (Hamon et al., 2008, 2002; Harper et al., 1998; Rodrigues et al., 2010; Zhang et al., 2004). Recently, Hamels et al. (2014) showed that the isotopically exchangeable fraction of the total soil metal in field-contaminated soils explained lower toxicity of metals as compared with spiked soils. The term “reactive” is based on the operational definition presented in Degryse et al. (2009) as metal in the solid phase that “equilibrates with the solution phase within a few days”. The reactive metal typically includes outer-sphere and weakly bound inner-sphere complexes on mineral surfaces or organic matter and should not be confused with the “chemically labile” metal (Sarret et al., 2004). The latter may include strongly sorbed inner-sphere complexes which are chemically reactive, but not necessarily available for solid-liquid partitioning within a time scale of days (Hamon et al., 2008). Reversible transformations between chemically labile (but often non-reactive) and reactive metal pools can occur, implying that the size of the reactive fraction in soil can change with the aging time. The reactivity of a metal in soil can vary depending on the anthropogenic source from which it is emitted (Degryse et al., 2004; Roberts et al., 2002; Vespa et al., 2010) and furthermore it can increase with time due to weathering (resulting in destruction of chemical bonds, most often those between metal and oxygen) (Casey et al., 1993) or it can decrease with time due to fixation in the soil through short- and long-term reactions with soil constituents (Buekers et al., 2008b; Crout et al., 2006; Ma et al., 2013, 2006; Wendling et al., 2009).

To accommodate these potentially important influences on the metal ecotoxicity in LCA, some modifications and further developments of the methodology are needed: (i) in the LCI phase, metal emissions should be reported together with sufficient information to allow capturing the differences that exist in reactivity between the various chemical forms that are present in the emissions from different sources; (ii) in the LCIA phase, CTPs for the metal of interest have to be available that match the information from the emission inventory and represent the ecotoxicity potential of the different metal forms; and (iii) in the LCIA phase, such a set of CTPs for the metal of interest has to consider metal aging in the soil, as influenced both by soil properties and by the aging pattern exhibited by the different metal forms reported in the LCI phase.

The aim of our study is to present the methodology needed to improve current LCI and LCIA practice in terrestrial ecotoxicity assessment of metals in soil, and to make it operational for the metals Cd, Co, Cu, Ni, Pb, and Zn. We first present a conceptual aging model for metals in soils and propose a framework for inclusion of aging in calculation of CTPs of metals in soils. In the second part of the study, we determine the important factors for the reactivity of the six metals

(such as metal emission source, soil properties, aging time in the soil, and the rate of water exchange on metal ions) based on empirical data from an extensive literature review, and show how reactivity affects CTP of the studied metals. The empirical data represent particle-bound metal in fly ashes, metal occluded in biosolids and other organic matrices, and metal released from mining activities or industrial waste, which together constitute the major sources of anthropogenic metals in soils (Nicholson et al., 2003). The age of the man-made metal contamination in many cases had to be assumed and is therefore uncertain. Furthermore, the availability of measured data for some potentially important soil properties, is limited. Therefore, insights into aging mechanisms had to be gained by comparison with metal reactivity measured in soils spiked with soluble metal ion salts and soils contaminated with geogenic metal, and by comparison with predictions of existing kinetic aging models and empirical regression models.

115

116 2. Methods

117 2.1. Definitions and Presentation of a Conceptual Aging Model for Metals in Soil

118 Aging of a Metal in Soil is defined as “change in solid-phase reactivity of a metal in soil over time”.
119 This includes fixation that reduces metal reactivity (up to now referred to just as “aging” for soils
120 spiked with soluble salts), and weathering that potentially increases metal reactivity in soils.

121

122 Time-Dependent Reactive Fraction of a Metal in Soil (f_{reactive} , $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$) represents the
123 fraction of total metal in soil at that is available for solid-liquid partitioning within a time scale of
124 days as it varies with the aging time t (in years) of the metal in the soil (eq 1).

$$125 \quad f_{\text{reactive}}(t) = \frac{C_{\text{reactive}}(t)}{C_{\text{total}}(t)} = \frac{s_{\text{reactive solid}}(t) + L/S \cdot c_{\text{total dissolved}}(t)}{s_{\text{total solid}}(t) + L/S \cdot c_{\text{total dissolved}}(t)} \quad \text{eq 1}$$

126 where $C_{\text{reactive}}(t)$ ($\text{kg}_{\text{reactive}}/\text{kg}_{\text{soil}}$) and $C_{\text{total}}(t)$ ($\text{kg}_{\text{total}}/\text{kg}_{\text{soil}}$) are the concentrations of reactive metal
127 and total metal in soil at time t (year), respectively; $s_{\text{reactive solid}}(t)$ ($\text{kg}_{\text{reactive solid}}/\text{kg}_{\text{solid}}$) and $s_{\text{total solid}}(t)$
128 ($\text{kg}_{\text{total solid}}/\text{kg}_{\text{solid}}$) are the concentrations of reactive metal and total metal in the solid phase at time
129 t , respectively; $c_{\text{total dissolved}}(t)$ ($\text{kg}_{\text{total dissolved}}/L_{\text{pore water}}$) is the concentration of total dissolved metal
130 (assumed reactive) in soil pore water at time t ; and L/S ($L_{\text{pore water}}/\text{kg}_{\text{soil}}$) is the ratio of pore water
131 volume to soil mass.

132

133 Conceptual Aging Model for Metals in Soil. Figure 1 illustrates the temporal evolution of the
134 reactive fraction of a metal in a soil that is either spiked with readily soluble salt of the metal or is
135 contaminated with an anthropogenic non-reactive form of the metal. The evolution is predicted

136 using a three-compartment conceptual aging model, developed from a two-compartment model
137 presented by Crout et al. (2006). The model takes into account reversible, exchange between
138 reactive and nonreactive (but chemically labile) compartments, obeying first-order kinetics. In
139 addition, to capture long-term aging mechanisms, an additional irreversible first order exchange
140 between nonreactive (but chemically labile) and inert (chemically not labile) metal pools had been
141 incorporated (Amacher, 1991; Davis et al., 1994).

142 The model is conceptual as it does not take into account various processes that may alter the
143 shape of reactivity curves, such as the possibility of biphasic exchange kinetics, the presence of
144 several metal pools with pool-specific exchange rate constants, very slow release of a metal from
145 the inert metal pool, or mobilization of strongly bound metal phases in plant rhizosphere in the
146 events of nutrient deficiency (Hinsinger, 2001). Yet, it allows us to illustrate how temporal
147 developments of the reactive fraction may depend on the form in which the metal is emitted and on
148 rate constants for the fixation and weathering reactions. The reactive fraction of a readily soluble
149 salt of the metal is initially (at time t_0) equal to 1, but it can be reduced due to fixation into soil
150 constituents (t_0 to t_1). This fixation mechanism occurs readily in spiked soils (Buekers et al., 2007;
151 Crout et al., 2006). In contrast, the reactive fraction of an anthropogenic emission of the metal is
152 expected to be lower initially (equal to 0 in the extreme case, as was assumed here), but can
153 increase due to weathering (t_0 to t_1) and then decrease due to fixation (after t_1). For example,
154 weathering of metal sulfides (CdS, CuS, or PbS) in mine tailings through oxidation and dissolution
155 of the primary sulfide increases reactive fraction initially; metals will form reactive outer-sphere
156 and weakly bound inner-sphere complexes on mineral surfaces or organic matter (Ribeta et al.,
157 1995). If soil is limed to neutralize its acidity, however, metals will precipitate because of formation
158 of poorly-ordered (amorphous) oxides and/or carbonates that are not reactive. These poorly-ordered
159 minerals will over time change to well-ordered (crystalline) minerals that can be inert; time ranges
160 required to attain equilibrium for crystallization reactions in soils are in range of years to millennia
161 (Amacher, 1991; Sparks, 2000). The fixation of the non-reactive metal pool into the inert pool is
162 expected to further contribute to reduce the reactive fraction of anthropogenic metal at longer-time
163 scales (after t_1). On the other hand, if the soil is not limed, the reactive fraction is expected to
164 remain at a higher level as compared to limed soils (Ahnstrom and Parker, 2001; Li et al., 2014;
165 Nakhone and Young, 1993). If metal is occluded in solid particles (as e.g. ZnO in car tire debris),
166 the solid phase matrix in which the metal is emitted may influence weathering kinetics by slowing
167 down metal release from the matrix (Rhodes et al., 2012; Smolders and Degryse, 2002)

168 We hypothesize that after a certain time t_1 long-term aging mechanisms will eventually lead to
169 formation of the same chemical forms in the soils, regardless of the initial emission source, and it

will no longer be possible to distinguish between metals from spiked and anthropogenic sources. This time may be several hundreds or thousands of years, depending on the dominant aging mechanisms and their rates. If metal forms in the soil at t_1 are the same regardless the initial emission form of the metal, aging mechanisms that occur after t_1 will be the same. We also hypothesize that as aging time goes toward infinite time, metal reactivity may become equal to the reactivity of the metal constituting the geogenic background. This is because metal forms derived from either initial form of the metal may over very long (sufficient) time end as the same as in the background and it will no longer be possible to distinguish whether the metal is geogenic or from an anthropogenic emission. In practice, this situation may never be reached, as processes that influence the ultimate fate of the soil such as erosion by surface water or glacial events, will also determine the ultimate fate of metal present in the soil. However, Vespa et al. (2010) showed that Zn phyllosilicate species formed from smelter-related ZnS and ZnO were analogous to the native phyllosilicate species which formed over time during pedogenesis.

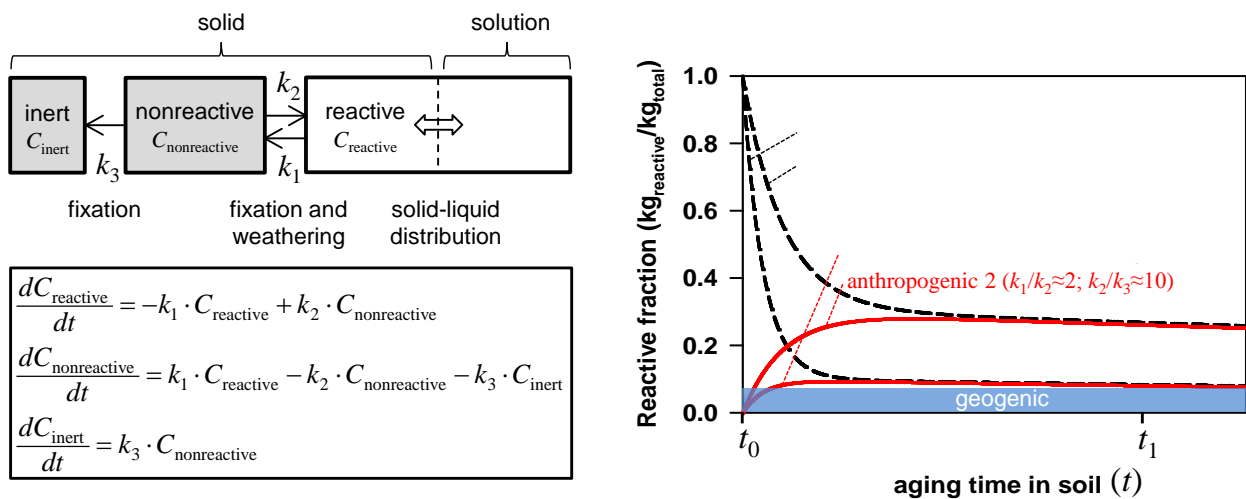


Fig. 1. Left panel shows a three-compartment conceptual aging model for metals in soil; right panel shows predicted evolution of the reactive fraction ($f_{reactive}$, in $kg_{reactive}/kg_{total}$) of a metal in soil spiked with readily soluble metal salt assumed to be 100% reactive initially (black dashed lines), and in soil contaminated with metal from an anthropogenic source (red lines) assumed to be 100% nonreactive initially, shown against the background reactivity of geogenic metal. Predictions are shown for two sets of first order exchange rate constants for the fixation and weathering reactions (k_1 , k_2 and k_3 , in day^{-1}).

2.2. Framework for Inclusion of Aging in Calculation of Comparative Toxicity Potentials of Metals in Soils

194 Time-Horizon Dependent Accessibility Factor of a Metal in Soil (ACF^T , $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$) represents
 195 the reactive fraction f_{reactive} integrated over the metal's aging time t (in years) in the soil, from $t=0$ to
 196 $t=T$ (where T is the chosen time-horizon, in years) divided by the T (eq 2). This definition of the
 197 ACF builds on that proposed earlier in Owsianiak et al. (2013) where ACF was assumed equal to
 198 (time-independent) f_{reactive} and no time-horizon dependency of the ACF was considered.

$$199 \quad ACF^T = \frac{\int_0^T f_{\text{reactive}}(t) dt}{T} \quad \text{eq 2}$$

201 Time-Dependent Distribution Coefficient between Total Solid Phase and Solution Phase

202 ($K_{\text{d,total}}(t)$, in $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$) is calculated from the time-dependent solid-phase reactivity of the
 203 metal and its time-independent distribution coefficient between reactive solid phase and solution
 204 phase ($K_{\text{d,reactive}}$, in $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$) (eq 3). Because the amount of metal in solution ($L/S \cdot c_{\text{pore water}}$ in
 205 eq 1) is usually very small in soils compared with the total metal concentration (Bueckers et al.,
 206 2008a) this solid-phase reactivity can be approximated by f_{reactive} .

$$207 \quad K_{\text{d,total}}(t) = K_{\text{d,reactive}} \cdot \frac{s_{\text{total}}(t)}{s_{\text{reactive}}(t)} \approx \frac{K_{\text{d,reactive}}}{f_{\text{reactive}}(t)} \quad \text{eq 3}$$

209 Time-Horizon Dependent Distribution Coefficient between Total Solid Phase and Solution Phase (

210 $K_{\text{d,total}}^T$, in $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$; eq 4) can be applied for calculating time-horizon dependent fate factors
 211 (FF) to compensate for the fact that time-dependent partitioning is not considered in existing
 212 multimedia fate models.

$$213 \quad K_{\text{d,total}}^T \approx \frac{K_{\text{d,reactive}}}{ACF^T} \quad \text{eq 4}$$

214 Time-Horizon Dependent Comparative Toxicity Potential (CTP_c^T , in $\text{m}^3/\text{kg}_{\text{total emitted}} \cdot \text{day}$; eq 5) of a
 215 metal in soil after a unit emission to compartment c for the time horizon T , is calculated as
 216 (Owsianiak et al., 2013):

$$217 \quad CTP_c^T = FF_c^T \cdot ACF^T \cdot BF \cdot EF \quad \text{eq 5}$$

218 where FF_c^T (in days) is the time-horizon dependent fate factor in soil calculated for total metal
 219 emitted to compartment c calculated using $K_{d,total}^T$ values; ACF^T ($\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$) is the time-
 220 horizon dependent accessibility factor; BF ($\text{kg}_{\text{free}}/\text{kg}_{\text{reactive}}$) is the time-horizon independent
 221 bioavailability factor defined as the free ion fraction of the reactive metal in soil, and EF ($\text{m}^3/\text{kg}_{\text{free}}$)
 222 is the time-horizon independent terrestrial ecotoxicity effect factor defined as potentially affected
 223 fraction (PAF) of species for the free ion form of the metal.⁴³

224 Metal aging will influence CTP of a metal through its control of both fate and accessibility. A
 225 reduction in reactive fraction increases $K_{d,total}^T$ and thereby the FF, because metal's residence time in
 226 soil increases with an increase in $K_{d,total}^T$ (Owsianiak et al., 2013). This leads to increasing the CTP.
 227 On the other hand, a reduction in reactive fraction reduces the ACF, which leads to decreasing the
 228 CTP. These two effects only partly compensate each other, because metal fate in soil also depends
 229 on the loss of the soil to surface water through soil erosion. The influence of metal aging on CTP is
 230 expected to be higher for those metals, for which $K_{d,reactive}$ is high. To illustrate this, we compared
 231 CTPs calculated for the infinite time horizon assuming reactive fraction equal to 1 $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$,
 232 with the CTPs calculated for the ACFs derived from reactive fractions as determined in the current
 233 study (which were always below 1 $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$). The FFs were calculated employing USEtox
 234 using $K_{d,total}$ values estimated from $K_{d,reactive}$ and the corresponding ACFs (eq 4), assuming default
 235 values of 0.03 mm/yr for the soil erosion rate and 0.1 m for soil depth (Rosenbaum et al., 2008).
 236 Details of the calculations are presented in Appendix 1, Section A5.

$$237 \quad \frac{CTP_{ACF=f(f_{\text{reactive}})}}{CTP_{ACF=1}} = \frac{FF_{ACF=f(f_{\text{reactive}})} \cdot ACF_{ACF=f(f_{\text{reactive}})} \cdot BF \cdot EF}{FF_{ACF=1} \cdot 1 \cdot BF \cdot EF} = ACF_{ACF=f(f_{\text{reactive}})} \cdot \frac{FF_{ACF=f(f_{\text{reactive}})}}{FF_{ACF=1}} \quad \text{eq 6}$$

238

239 2.3. Data Collection and Treatment

240 Metals were included if data on reactive fraction for at least two different emission sources could be
 241 found. We thus included Cd, Co, Cu, Ni, Pb and Zn, and excluded Ag, Al and Fe (Collins and
 242 Waite, 2009; Gabler et al., 1999; Settimo et al., 2014). Data for the three latter were, however, used
 243 to see if our findings about factors controlling metal reactivity in soils apply also to other metals.
 244 Data were retrieved from peer-reviewed studies available until April 2013 identified through
 245 searching the ISI Web of Knowledge, version 5.7 (Thomson Reuters, New York, NY), using a
 246 combination of keywords: (i) isotop*; and either (ii) exchang*, or dilute*; and either (iii) labil*, or
 247 soil*; and either (iv) Cd, Co, Cu, Ni, Pb, Zn, cadm*, cobalt*, copp*, nick*, lead, or zinc*. A
 248 complementary search was conducted in ISI to retrieve publications citing references retrieved in

the previous step, and those which were cited in the collected publications, but were not found through the initial search in ISI. The two latter steps were iterated until no new data were found. A study of Degryse et al. (2004) containing data on reactivity of various anthropogenic forms of Cd and Zn is excluded and was used to compare our results with their findings, as is a recent study of Marzouk et al. (2013) containing data on reactivity of anthropogenic forms of Cd, Pb and Zn that was published after the searching had been done. Data were included if the following criteria were met: (i) emission source was reported; (ii) reactive fraction or reactive concentration were measured in soils; and (iii) reactive fraction or reactive concentration were measured using isotope dilution methods. The last criterion was applied to minimize uncertainties associated with the determination of the concentration of reactive metal in soil; others showed the lack of correspondence between metal fractions extracted using sequential extraction procedures and the size of reactive metal pool measured using isotope-based methods (Ahnstrom and Parker, 2001). We combined methods that measure either isotopically exchangeable (comprising reactive metal in the solid-phase only) or isotopically available (comprising reactive metal both in the solid phase and in the soil solution) pools to increase the number of data. This can introduce an error of >10% if soil sorption capacity is low (Hamon et al., 2002). Details of harmonization of soil properties and descriptive statistics are presented in Appendix A, Section A1.

Classification of Emission Sources. Data were first classified into three major categories: (i) “spiked” for soils spiked with soluble salts; (ii) “anthropogenic” for soils contaminated with primarily solid-phase metal of anthropogenic origin, excluding nanoparticles and massive products such as Cu ingots which are outside the scope of this study; and (iii) “geogenic” for soils contaminated with primarily solid-phase metal forms of geogenic origin.

Anthropogenic emissions that originate from similar processes or are similar with regard to the composition of the matrix surrounding the metal in the emission are expected to have similar chemical composition. For example, metal oxides are typically created during combustion processes in power plants, smelters or incinerators, mining-related metal emissions can contain a large proportion of metal sulfides, while metals found in biosolids or those found in wastewater are likely to be found in association with organic carbon. It is thus hypothesized that statistically significant differences in reactive fraction between these emissions source classes can be found. Therefore, the “anthropogenic” category was further classified into four subcategories: (i) “airborne” including emissions from smelters, metal refineries, factories, combustion of petrol, and unspecified atmospheric deposition; (ii) “organic-related” including direct application of biosolids, manure, compost, or wastewater irrigation; (iii) “mining and industrial waste” including emissions from

mine spoils, mining-affected sediment, material containing metal ores, alluvial deposition, unspecified industrial waste, and technosols; and (iv) “other anthropogenic” including emissions from ZnO (isolated or in tire debris), mixed anthropogenic sources, unspecified anthropogenic sources, and dissolved metal forms of anthropogenic origin (such as Cd present as a co-contaminant in phosphate fertilizer or Cu sulfate applied as a fungicide, or aqueous Zn dissolving from galvanized power lines). It was assumed that if one emission source was given in the respective publication, that source was the sole metal source in the soil. Mixed anthropogenic sources were classified as other anthropogenic because no information could be retrieved about the dominant metal source in the included soils. Note, that in contrast to many studies for readily soluble salts, metal reactivity in anthropogenically contaminated soils cannot be attributed exclusively to anthropogenic sources because reactivity of geogenic metal prior to anthropogenic input is not known.

295

Estimation of Aging Time in Soil. A metal's aging time in soil (ideally) represents the time that the metal has been in soil prior to the measurement of its reactivity. To get more insight into the influence of contamination age on metal reactivity for anthropogenic sources, we often had to make assumptions about the age by setting it equal to the time from the emission peak to the publication year, or equal to half of the time interval between start and termination of the emission (if emission peak was not reported). If an emission was reported to have occurred for more than or less than a certain time period, contamination age was assumed equal to the starting date plus double or half the length of that time period, respectively. If only a century of emission start was reported, time from the middle of that century to publication year was assumed as the age. If the emission source could be unambiguously identified, and information on contamination age could be retrieved from sources reporting emission data this information was used as the contamination age for that source. Acknowledging the uncertainty in estimating the age, the anthropogenic contaminations were classified into 5 age groups: (1) from 0 to 20 years; (2) from 20 to 50 years; (3) from 50 to 100 years; (4) from 100 to 150 years; and (5) from 150 to 220 years. Spiked soils, where aging time is certain, were classified into 2 age groups: (I) from 0 to 0.5 years; and (II) from 0.5 to 2.5 years.

311

2.4. Analysis of Covariance (ANCOVA) and Wilcox Procedures

To increase the opportunity to find statistical significance of the effects of metal emission source on reactive fraction while controlling for the effect of given soil property, we used one-way analysis of covariance (ANCOVA), as explained in Appendix A, section A2. ANCOVA models were expressed as ordinary least squares (OLS) regression models with the metal source term coded

317 employing the effect coding system and a given soil property being a covariate. If non-constant
318 variance related to the source term was identified, weighted least squares (WLS) regression was
319 employed with weights being based on the metal source. Models were developed for each soil
320 property separately. Logit-transformation of f_{reactive} was done when it improved normality of
321 distribution of the independent variable (in practice for all metals except of Cd), consistently with
322 the ANCOVA assumption, and was chosen among other transformation types as it an appropriate
323 transformation option for proportions. To identify where significant differences in (logit-
324 transformed, apart from Cd) f_{reactive} between metal emission sources occur, ANCOVA was followed
325 by post-hoc multiple comparison tests based on the Tukey HDS method (employing the glht
326 function available in the R package multcomp) controlling for the soil property explaining the
327 largest part of the variance in the (logit-transformed, apart from Cd) f_{reactive} . In cases where
328 regression slopes were not homogeneous, the Wilcox modification of the Johnson-Neyman (J-N)
329 procedure was performed for pairwise comparisons as it allows identifying ranges of a soil property
330 where significant differences in metal reactivity between emission sources occur. Similarly, to test
331 for the effect of aging, pairwise comparisons between age groups for each anthropogenic source.
332 Comparisons were also made between anthropogenic sources and the two age groups for spiked
333 soils. OLS and WLS regression models were developed by R version 3.1.2 (R Core Team, Vienna,
334 Austria). The Wilcox procedure was executed using the program WILCOX.exe written by
335 Constable. Details of the analyses are presented in the Appendix A, Section A2.

336

337 **3. Results and discussion**

338 Below, we show how reactive fraction depends on emission source and aging time in the soil. We
339 also show how it relates to a metal-specific property, the metal's water exchange rate constant.
340 Implications of our findings for reporting and impact assessment of anthropogenic metal emissions,
341 are then discussed.

342

343 *3.1. Does Emission Source Matter?*

344 Figure 2 (left panel) shows the variability in the reactive fraction of the metals as influenced by
345 metal source. One-way ANCOVA and WILCOX procedures revealed statistically significant
346 differences between geogenic and various anthropogenic forms of Cd, Co, Cu and Zn (Table 1)
347 when the covarying effects of soil pH or soil organic carbon are taken into account. Across these
348 metals, anthropogenic sources generally have higher reactive fraction as compared to geogenic
349 metals forms, apart from Cd where the opposite is the case. No differences were found between

350 geogenic and various anthropogenic sources for Ni and Pb. Between anthropogenic forms of Cd,
351 Co, Cu and Zn, statistically significant differences in the reactive fraction were found occasionally.
352 Again, no differences were found between anthropogenic sources for Ni and Pb.

353 A significant effect of anthropogenic metal source on reactive fraction of the studied metals
354 was not unexpected, particularly for Zn where the differences in reactive fraction were the most
355 apparent. Molina et al. (2013) showed that reactivity of Zn in pure-phase minerals and mine waste
356 varied between chemical forms of Zn. Also Degryse et al. (2011) showed that Zn layered double
357 hydroxide (Zn-LDH) and Zn in hydroxy-interlayered minerals (Zn-HIM), which are common forms
358 of Zn in soils, had relatively low reactivity compared to other common forms of Zn, such as zinc
359 carbonate (ZnCO_3) and hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$). The differences in reactive fraction of
360 different forms of Zn can be explained by their differences in resistance to proton-promoted
361 dissolution. This is supported by the fact that we found a small negative effect of soil pH on
362 reactivity of Zn, and may suggest that the soils included contained forms of a metal that are not
363 resistant to proton-promoted dissolution, such as Zn-LDH or carbonates, with relatively small
364 contribution of forms more resistant to proton-promoted dissolution, such as Zn-HIM (Degryse et
365 al., 2011; Khaokaew et al., 2012). Jacquat et al. (2009) showed that Zn in primary smelter minerals
366 accounted for only 5% of total Zn in the bulk soil.

367 In many cases we found no consistent effect of emission source on reactivity of other sources
368 and metals. This could be partly explained by low number of data points for individual emission
369 sources, combined with limited information on potentially relevant soil parameters, such as content
370 of Al or Mn (hydr)oxides that were not available for all data points collected. Differences in
371 reactive fraction between metal sources due to differences in resistance to proton-promoted
372 dissolution of metal forms could be expected for other metals as well (Peltier et al., 2010; Voegelin
373 and Kretzschmar, 2005), and we did find a small negative effect of soil pH on the reactivity of Cd,
374 Cu, and Pb. Yet, for Ni and Pb we did not find any differences between anthropogenic and geogenic
375 sources at all. This might be because metal forms in the emitted material either transform to forms
376 for which reactivity is close to the reactivity of the geogenic background, or transform to forms
377 constituting the geogenic background. Ettler et al. (2012) showed that dissolution of primary Pb
378 minerals (caracolite and K-Pb chloride) in a smelter fly ash led to formation of secondary anglesite,
379 minor Pb sulfate, and trace cerussite in soils, whereas about half of total Pb originating from mine
380 tailings and smelters was included in Fe- and Mn-(oxyhydr)oxides (Morin et al., 1999) which are
381 common geogenic forms of Pb (Teutsch et al., 1999). Published regression models developed for
382 soils contaminated with anthropogenic and/or geogenic metal generally predict reactive metal
383 concentrations within one order of magnitude around the measured values (see Appendix 1, Section

384 A4). Thus, the published models do not allow distinguishing between various anthropogenic
385 contamination forms as the error of prediction of the reactive fraction for the six studied metals
386 using any regression model is similar to the variability in the reactive fraction that is also within one
387 order of magnitude (see Appendix 1, Section A4). This supports our findings about some
388 difficulties to capture influence of contamination form on reactivity of anthropogenic metals in
389 soils.

390 Reactive fraction of Cd, Cu, Pb and Zn generally decreases with soil pH. Reactivity of Co and
391 Ni increases with an increase in organic carbon content of the soil but for Cd regression slopes are
392 not homogeneous; reactivity of organic-related Cd is significantly different from that measured for
393 both airborne and geogenic sources of Cd in acidic soils (pH<6.2) only (Table 1). These findings
394 are in agreement with Marzouk et al. (2013) who also found a negative effect of soil pH on
395 reactivity of Cd, Pb and Zn for a large set of 246 mining-impacted soils, and also in agreement with
396 Degryse et al. (2004) who found weak correlations between pH and reactive Zn in soils for a set of
397 74 soils contaminated with metals from various sources. By contrast, Degryse et al. (2004) did not
398 find any pH effect for Cd. We also found a small positive effect of soil organic carbon on reactivity
399 of Co and Ni. Differences in number of soils included for the different metals, combined with the
400 associated differences in property ranges between the soils in our data set may also explain why we
401 are not able to see any influence of organic carbon for Cd, Cu, Pb and Zn. Metals bound to organic
402 carbon are generally reactive in soils (Sarret et al., 2004), but soils spanning a rather wide range of
403 soil organic carbon content are needed to capture the relationship (Marzouk et al., 2013).

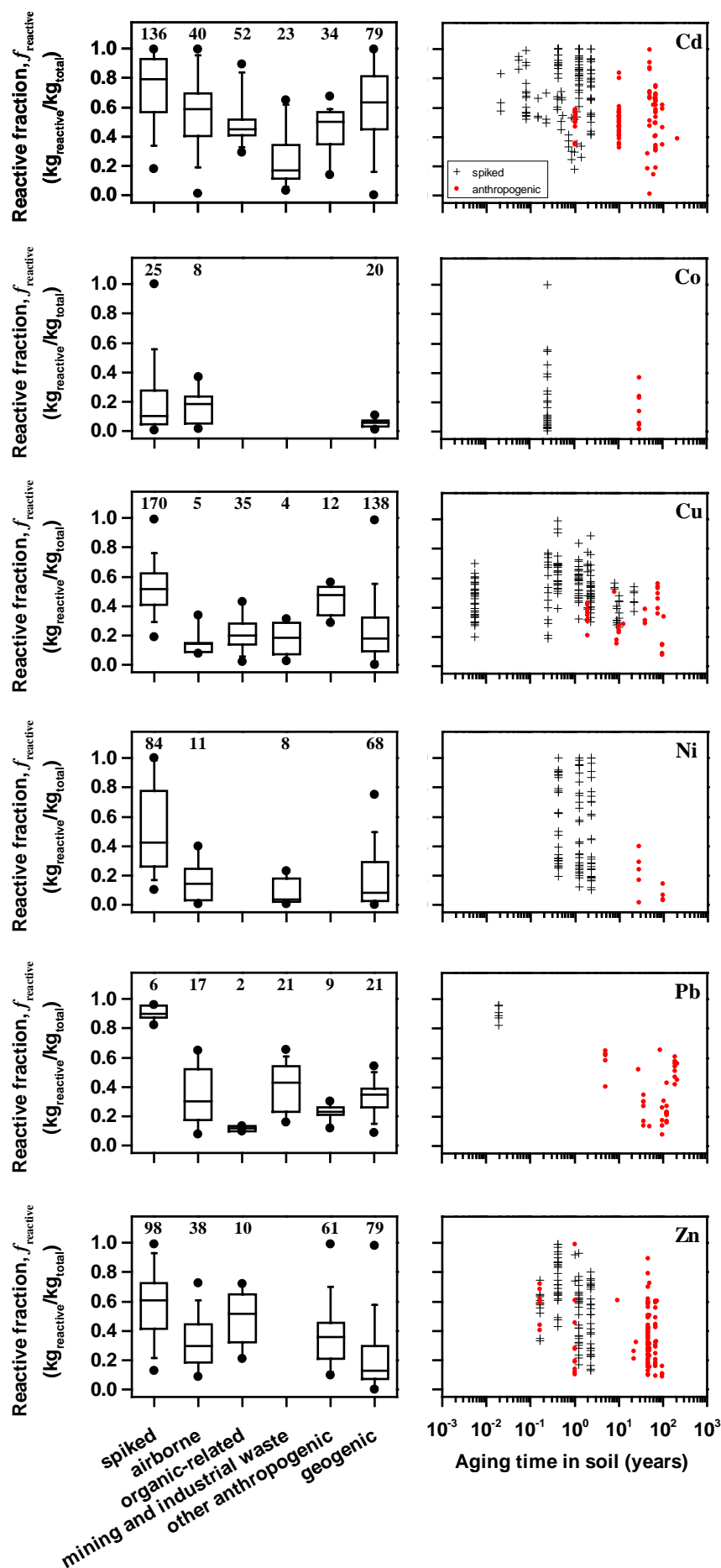
404

405 3.2. Does Aging Matter?

406 Figure 2 (right panel) shows the variability in the reactive fraction of the studied metals as
407 influenced by contamination age for the anthropogenic emission forms. There was no consistent
408 effect of aging in reactive fraction. There is a statistically significant difference between Pb aged for
409 100-150 years and Pb aged for 150-220 years (with the latter being more reactive), but there is no
410 statistically significant difference between airborne Cd aged for 20-50 years and airborne Cd aged
411 for 50-100 years. The difference between airborne Cd aged for 20-50 years and that aged for 50-100
412 years depends on soil pH, however, and there is no difference in the pH range 4.1 – 6.9. Due to
413 missing information about aging time for many data points for anthropogenic sources, statistical
414 comparison for other metals and sources was not possible.

415 Reactive fractions in spiked soils aged for up to 0.5 year were significantly higher than those
416 measured for geogenic and various anthropogenic sources, irrespective of the anthropogenic source
417 and its age (see Table 2 and Appendix A, Section A3). The difference in reactive fraction between

418 spiked soils aged for more than 0.5-2.5 years and anthropogenic sources was smaller, but remained
419 statistically significant for organic-related Cu and airborne Zn. This is probably because such short-
420 term (< 2.5 years) experiments in spiked soils do not allow for occurrence of long-term aging
421 mechanisms, such as precipitation of salts or formation of non-reactive minerals of lower reactivity
422 (Amacher, 1991). This is in agreement with Ma et al. (2013), who showed how a kinetic aging
423 model overestimates reactivity of Ni in field-contaminated, agricultural and serpentine soils. By
424 contrast, the difference in reactive fraction between spiked soils aged for 0.5-2.5 years and
425 anthropogenic sources was not statistically significant for airborne Cd, other anthropogenic forms
426 of Cu, and organic-related Zn (see Table Ax and Figure Ay). For Cd, this reflects a rather high
427 reactivity of Cd in soils and can mainly be explained by the fact that Cd is mostly present in soil
428 solutions in dissolved forms as free ions or labile complexes which bind to soil constituents through
429 weak electrostatic forces (Rodrigues et al., 2010). Chrastny et al. (2012) and Nowack et al. (2010)
430 also reported higher amounts of weakly bound, reactive Cd in organic-rich soils contaminated with
431 Cd originating from a smelter. The other anthropogenic forms of Cu (being wood impregnate and a
432 fungicide) contained readily soluble Cu sulphate that had aged for several decades in field
433 condition, while some of soils spiked with Cu were leached. This may explain the lack of statistical
434 difference in the reactive fraction between these sources, as leaching is expected to reduce reactive
435 fraction in spiked aged soils as compared to non-leached aged soils (Ma et al., 2006). This may
436 suggest that in some cases aged spiked soils can be used to approximate reactive fraction for
437 anthropogenic metals. To test this, we systematically assessed the performance of published kinetic
438 aging models that were developed for soluble salts for prediction of reactivity for anthropogenic
439 contaminations in soils (see Appendix A, Section A4). The comparison of measured concentrations
440 of reactive metal and concentrations predicted by published kinetic aging models shows that even if
441 infinite aging time is assumed, the calculated bias (that is, mean of residuals) is positive, indicating
442 that the models overestimate reactive concentration (and thus reactive fraction) of anthropogenic
443 metals. This highlights the need for considering differences in metal reactivity between spiked soils
444 and man-made metal contaminations soils in characterization of metal accessibility in soils.



446 Fig. 2. Left panel: reactive fraction (f_{reactive} , in $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$) of Cd, Co, Cu, Ni, Pb and Zn measured in soils spiked
447 with soluble metal salts and in soils contaminated with various anthropogenic or geogenic metals; boxes with bars
448 indicate the 5th, 25th, 50th, 75th, and 95th percentiles and black dots indicate minimum and maximum values; numbers
449 of data points per emission source are shown above the boxes. Right panel: reactive fraction of Cd, Co, Cu, Ni, Pb and
450 Zn measured in soils spiked with soluble metal salts (black crosses) and in soils contaminated with various
451 anthropogenic metals (where all anthropogenic emission sources are combined; red circles) in relation to aging time in
452 soil. Note, that the data presented are not corrected for geogenic background. Please see Table A1 and A2 for data
453 corrected for geogenic background that are available for some spiked soils.

454 Table 1. The analysis of the effects of metal source, soil properties, and aging on the reactive fraction and proposed
 455 reactivity rankings based on pairwise Tukey HSD or WILCOX comparisons (please see Tables Ax and Ay for details). The
 456 symbols < and > both indicate statistically significant difference between sources; \approx indicates either no statistically
 457 significant difference or that comparison could not be done (because standardized residuals are related to the covariate or
 458 because Q-Q plot for standardized residuals shows unacceptable deviations from 1:1 line); $< \approx >$ indicate that statistical
 459 significance and direction of the difference depend on soil pH (for Zn) or soil organic carbon (for Co) values.

F statistics for one-way ANCOVA models		Proposed reactivity ranking based on pairwise Tukey HSD and WILCOX comparisons
Geogenic and anthropogenic sources irrespective of aging time:¹		
Cadmium		
pH _{H2O}	F _{1,218} =22.7, p=3e-06	m&w ≈ organic ≈ other < airborne ≈ geogenic
Source	F _{4,218} =7.04, p=2e-05	
Source×pH _{H2O}	F _{4,218} =4.87, p=0.0009	
Cobalt		
log ₁₀ (OC) ⁴	F _{1,23} =5.39, p=0.29	geogenic < airborne
Source ⁴	F _{1,23} =6.03, p=3e-5	
Copper⁴		
pH _{H2O} ⁴	F _{1,181} =33.6, p=3e-8	geogenic ≈ organic < other
Source ⁴	F _{2,181} =34.5, p=2e-13	
Nickel		
log ₁₀ (OC) ⁵	F _{2,85} =12.7, p=0.0006	geogenic ≈ m&w ≈ airborne
Lead		
pH _{H2O} ⁵	F _{1,66} =67.2, p=1e-11	geogenic ≈ m&w ≈ airborne ≈ other
Zinc		
pH _{H2O} ⁴	F _{1,171} =67.2, p=1e-11	geogenic < airborne < other ≈ organic
Source ⁴	F _{3,171} =14.2, p=3e-8	
Spiked soils and anthropogenic sources as influenced by aging time:²		
aging time for spiked soils: I (0-0.5 yr); II (0.5-2.5 yr) aging time for anthropogenic sources: 1 (0-20 yr); 2 (20-50 yr); 3 (50-100 yr); 4 (100-150 yr); 5 (150-220 yr)		
Cadmium		
models were not developed	airborne(3) ≈ airborne(2) ≈ spiked(II) < ≈ > spiked(I)	
Cobalt		
models were not developed	airborne(2) < ≈ > spiked(I) not corrected	
Copper		
models were not developed	organic(1) < spiked(II) < spiked(I) other(3) ≈ spiked(II) < spiked(I)	
Nickel		
models were not developed	airborne(2) < spiked(I)	
Lead		
models were not developed	airborne(2) ≈ airborne(1) < spiked(I) m&w(4) < m&w(5) < spiked(I)	
Zinc		
models were not developed	airborne(3) < ≈ > airborne(2) < spiked(II) ≈ spiked(I) other(1) ≈ spiked(II) ≈ spiked(I)	

¹ m&w, organic and other represent the “mining and industrial waste”, “organic-related” and “other anthropogenic” metal sources, respectively

² soils spiked with Co and Pb are not corrected for geogenic background due insufficient number of data points for which such correction could be done to make the comparison possible.

3.3. Metal Reactivity In Relation to the Intrinsic Kinetic Lability of Metal Ions

According to the conceptual aging model presented in Fig. 1, the size of reactive fraction depends on the exchange rate constants for the fixation and weathering reactions. The fixation rate constants are mainly determined by soil pH (Buekers et al., 2008b; Crout et al., 2006; Ma et al., 2013, 2006; Wendling et al., 2009). However, while the pH can also influence weathering kinetics, the weathering rate constants are expected to be mainly determined by the kinetic lability of metal ions as it determines the speed of a metal to undergo substitution reaction and thus desorption from the solid phase (Martell, 1978). Laird et al. (2011) already showed that metal bioaccessibility for gastrointestinal uptake from contaminated soils was related to a metal-specific property, the water exchange rate constant on metal aqua complexes (k_{H_2O}), whereas Owsianiak et al. (2014) showed that a parameter related to the k_{H_2O} was related to metal absorption efficiency in terrestrial worms exposed to aged soil contaminations. In this study, the k_{H_2O} can explain 63 and 49% of variability in average (geometric mean) reactive fraction of anthropogenic and geogenic metal forms, respectively (Fig. 3). Because the mechanism by which a cation leaves a dissolving mineral surface is similar to the mechanisms of water exchange in the hydrated complex, the observed relation is expected to hold for those metals and contamination forms, for which the major chemical bond in the contamination material is that between metal and oxygen (Casey and Westrich, 1992; Casey et al., 1993; Ludwig et al., 1996; Pokrovsky and Schott, 2002). Indeed, the average reactive fraction of anthropogenic or geogenic Fe^{3+} and Cr^{3+} in soils agrees with predictions of the two reactivity – lability relationships if extrapolated outside the six studied metals (Fig. 3). We thus suggest that regression models based on k_{H_2O} and can be developed to estimate reactive fraction for metals which form metal-oxygen bonds in soils. Their performance could potentially be improved by taking into account molecular diffusion of a metal ion along surface site in the soil, which could be related to acidity constants or radii of the metal ions (Axe and Anderson, 1997; Bruemmer et al., 1988). By contrast, any relationship based on k_{H_2O} is not expected to hold for metals, which do not tend to form metal-oxygen bonds in soils. Indeed, the average reactivity of Ag measured by Settimo et al. (2014) in soils spiked with soluble Ag salt aged for up to 6 months was smaller (from 50 to nearly 0%) than reactivity that could be expected based on the very large ($>1 \times 10^{10}$), unmeasurable k_{H_2O} of Ag^+ . This can be explained by the fact that the dominant forms of Ag in their soils were Ag bonded with S species, AgCl, and metallic Ag.

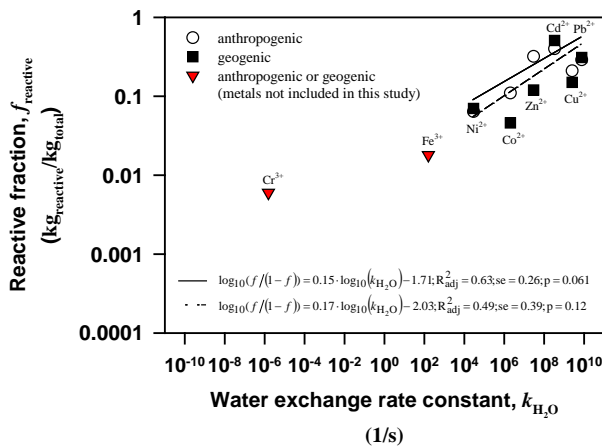


Fig 3. Relation between \log_{10} -transformed water exchange rate constant for metal aqua complexes, $k_{\text{H}_2\text{O}}$ (in 1/s) and logit-transformed, average (geometric mean) reactive fraction, f_{reactive} (in $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$) of Cd, Co, Cu, Ni, Pb, and Zn measured in soils contaminated with anthropogenic forms of the metals (white dots and solid line) and geogenic metals (black squares and dashed line). Red triangles show reactive fraction measured by Gabler et al. (1999) for Cr^{3+} ; and reactive fraction estimated for Fe^{3+} based on the data presented in Collins and Waite (2009) (averaged across 21 samples of an iron-rich acid sulfate soil, assuming that $C_{\text{total}} = 0.05 \text{ kg}_{\text{total}}/\text{kg}_{\text{soil}}$, which is in lower range of expected values; Richard Collins, personal communication). The $k_{\text{H}_2\text{O}}$ for metal ions were from Helm and Merbach (1999) except of Pb^{2+} , which was not available in the latter study, and was from Martell (1978).

3.4. Implications for Inventory Analysis and Reporting for Anthropogenic Metal Emissions

In current inventory practice of LCA and chemical hazard assessment, emissions of metals are reported as the element and its oxidation state (Pettersen and Hertwich, 2008; Pizzol et al., 2011). However, for four out of six metals we found statistically significant effect of the metal source on the reactive fraction, which suggests that for cationic metals the current practice may be insufficient to support the characterization of bioavailability and terrestrial toxicity. Therefore, to eliminate the potential error associated with using emission source-independent ACFs in calculation of CTP values of metals in soils, we propose that inventory procedures for metal emissions, such as applied in the LCI analysis phase of an LCA, should provide information about the metal emission source if that source is known. The proposed classification of emission sources into archetypes based on their expected differences in metal reactivities, may be used as guidance. The classification offers a compromise between on the one hand the unrealistic option of creating inventories of each chemical

species within a metal source (that would then have to be matched with metal species-specific CTPs), and on the other hand the currently prevailing practice of completely ignoring differences in the ACF (and thus CTP) between emission sources.

3.5. Implications for Impact Assessment of Metals on Terrestrial Environments

Our results suggest that at time scales of decades to centuries, the influence of aging on reactivity for anthropogenic metal sources is difficult to capture and is statistically uncertain. Thus, for calculating CTPs of cationic metals in soils we recommend using time-horizon independent ACFs derived from time-independent reactive fractions, combined with FFs calculated using time-horizon independent K_d^{total} values. If the emission source is known, ACFs should be derived from source-specific reactive fractions. If the emission source is unknown, ACFs can be derived from the geometric mean of the reactive fraction measured across all geogenic and anthropogenic contaminations in the study. Such a time-horizon independent ACF it is in practice equal to the (time-independent) reactive fraction and can be derived from values presented in Tables A1 and A2.

The implications of considering differences in reactive fraction on both fate and accessibility of the metals at the CTP level are presented in Fig. 4. For the metals Pb and Cu, the reduction in the CTP correlates almost linearly with the reduction in reactive fraction. These two metals are so strongly associated with the solid phase of the soil that their fate (residence time) in the soil is determined mainly by removal together with the solid phase, and this translates directly into the CTP (see eq 5). The CTP of Co and Ni is also reduced when reactive fraction decreases, particularly for the values below $0.5 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$, whereas for Zn the reactive fraction is only important in the lower range of values ($< 0.2 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$). For these metals, both leaching and erosion determine metal residence time in soils, and a decrease in ACF can partly be compensated by an increase in the FF. For Cd, a reduction in the reactive fraction (and thus ACF) has no influence on the CTP because its fate is determined primarily by leaching and a decrease in ACF is fully compensated by an increase in the FF. Note, that a USEtox-default value of 0.03 mm/yr was assumed for the soil erosion rate in calculation of fate factors. This value lies within the wide range of values determined for various soils (Montgomery, 2007), and implies that about 3300 years are required for a 10-cm top soil layer to exchange completely as a result of erosion and run-off loss to surface water. As many metals have strong affinity to soil constituents, this removal process is important in the overall fate, and further research should focus on providing solid data for soil erosion rates under different environmental conditions.

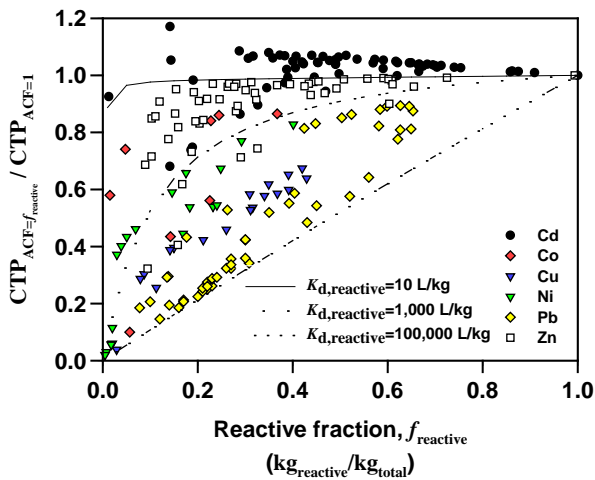


Fig. 4. Influence of the accessibility factor (ACF), as determined by the size of reactive fraction (f_{reactive}), on the comparative toxicity potential (CTP) of anthropogenic Cd, Co, Cu, Ni, Pb, and Zn in soils. Black solid and dashed lines represent three hypothetical cases for metals with $K_{d,\text{reactive}}$ equal to (i) 10; (ii) 1,000; and (iii) 100,000 $\text{L}_{\text{pore water}}/\text{kg}_{\text{soil}}$.

3.6. Limitations

The data set for anthropogenic sources is limited to contaminations aged for up to two centuries, and furthermore there is uncertainty in estimating the age. In the typically infinite time perspective applied in LCIA, aging processes may gain more importance by strengthening the binding of the metal in the soil and reducing its reactivity.. Considering the effort put into the literature search, it is questionable, however, whether a better data set can be compiled from the open literature, so it is not likely that such an aging effect can be demonstrated in this way. An alternative approach could be based on a repeated sampling experiment over centuries, but this is also not straight forward. On the other hand, in the assessment of CTPs for use in LCIA, the residence time of the metal in the soil may be restricted by the residence time of the soil solids in the soil compartment of the fate model, in which case even the aging over very long time perspectives will have small influence on the CTP values

Studies on metal reactivity in soils for other metals are scarce, which makes the estimation of reactive fraction, or any reactivity-age relationship, for the other metals virtually impossible. Reactive fraction could be potentially predicted using a structure-reactivity relationship, as demonstrated in this study for Cr and Fe. Alternatively, our conceptual aging model can be used to

determine shape of reactivity curve, provided that fixation and weathering rate constants are either measured or predicted for dominant soil minerals (Bearup et al., 2012; Brantley, 2008). A problematic issue is the estimation of the fixation rate constant between the inert and nonreactive (but chemically labile) metal pools, as is the potential for very slow release of metal from the inert pool that is not considered in our model and that may occur for some slowly-reacting minerals (Degryse et al., 2009).

4. Conclusions

We occasionally found the effect of the emission source on the solid-phase reactivity of the studied metals. The effect of contamination age in soil was not apparent, but the uncertainties in estimating the age do not allow drawing definite conclusions about the influence of aging time on the reactivity of anthropogenic metal sources in soils. We therefore recommend including the effect of the emission source and disregarding the role of aging in assessment of comparative terrestrial toxicity of anthropogenic Cd, Co, Cu, Ni, Pb and Zn. Our framework for including aging in calculation of fate and accessibility factors of metals in soils can, however, be used if aging is found to play a role in reactivity of other anthropogenic metals in terrestrial systems and if reactivity-age relationship can be estimated.

Appendix A. Supplementary data

Supplementary data related to this article can be found at [http:// dx.doi.org/](http://dx.doi.org/)

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Graphical abstract



Highlights

- we found an effect of source on reactivity of anthropogenic metals in soils
- the influence of aging on reactivity of anthropogenic metals was not consistent
- we recommend including source and disregarding aging in calculation of CTPs values